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Langmuir-Blodgett Films of An Amphiphilic Block Polymer Having Glucose Residues

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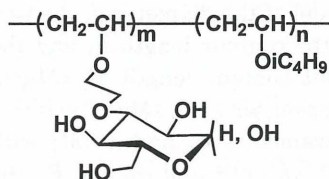
Amphiphilic block polymer **1** with a narrow molecular weight distribution was studied with its monolayer forming properties at the air-water interface. Polymer **1** and its blends with poly(isobutyl vinyl ether) homopolymer were found to form a stable monolayer on the water surface. The surface monolayers were successfully transferred onto a substrate by the Langmuir-Blodgett technique, and the built-up film was characterized by surface plasmon resonance and transmission electron microscopy. The observed values of the layer thickness and the occupied area indicated that the hydrophobic segments, which lie essentially flat on the water surface at lower surface pressures, aggregate at higher pressures, forming a thicker layer with hydrophobic and hydrophilic segments microphase-separated at the air-water interface.

Keywords: air-water interface / monolayer formation / structural transition / layered structure / microphase separation / blend LB film

Many studies have been focused on the synthetic polymers with pendant mono- and/or oligo-saccharide residues for various functions such as biodegradability, high water-absorbency, and surface and pharmacological activities. Most of them were synthesized by chemical modification of a conventional polymer or radical polymerization of a sugar-containing vinyl monomer. By these methods, however, it is very difficult to precisely control the chemical structure and macroscopic morphology of the polymer. Amphiphilic block copolymer **1**, newly synthesized in our laboratory by sequential living cationic polymerization,¹⁾ has a narrow molecular weight distribution of $M_w/M_n < 1.06$ and a controlled block composition. One of the two blocks of this copolymer consists of hydrophilic

repeating units containing a glucose residue, and the other is a poly(isobutyl vinyl ether) (PIBVE) block, which is hydrophobic. Since PIBVE has a monolayer-forming ability by itself, the block copolymer is expected to be fabricated into a glucose residue-carrying ultrathin film with a supramolecular structure by means of the Langmuir-Blodgett technique.

Polymer **1** with an appropriate segmental compo-



Block Copolymer **1**

P1($m/n=20/48$)

P2($m/n=20/89$)

ORGANIC MATERIALS CHEMISTRY — Polymeric Materials —

Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and development of novel functional polymers. Among those have been the studies on (1) the synthesis and properties of cellulose- and oligosaccharide-based functional polymers, e.g., bio-degradable polymers, liquid crystals and polymers of well-defined structure having pendant oligosaccharides, (2) the structure of polymer gels, ultrathin films and polymer alloys, and (3) the syntheses of new types of block and graft copolymers and fullerene(C_{60})-including polymers.



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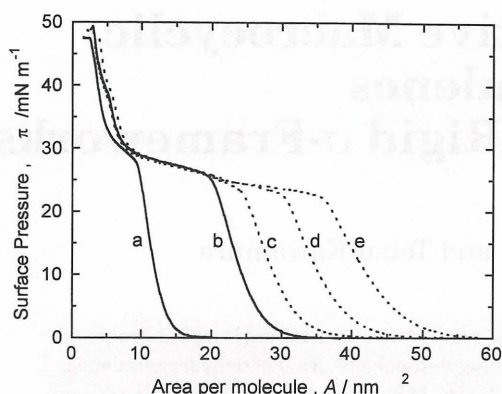


Figure 1. π - A isotherms of the block copolymers, (a) P1 and (b) P2, and the blends, PIBVE/P2 = (c) 0.10, (d) 0.25, and (e) 0.42

sition ($m/n = 20/48$ or $20/89$), spread from a mixture solution of methanol and chloroform onto the water surface, was found to form a stable monolayer. It was also possible to prepare a blend monolayer by spreading a mixture solution of the block polymer and PIBVE on the water surface. The surface pressure (π) - occupied area (A) isotherm for these surface monolayers measured at 10 °C are given in Figure 1, where A is the surface area per hydrophilic subchain in all cases. They exhibit a plateau region, suggesting a structural change taking place on the water surface at a specific pressure. With increasing number of the IBVE units in the copolymer and those blended as a homopolymer, the plateau region expands; A is proportional to n_T below the plateau pressures, where n_T is the total number of IBVE units divided by the number of the hydrophilic subchains, while A is almost constant at pressures above the plateau. From the n_T dependence of A , the occupied area per IBVE unit at 20 mN/m (below the plateau) was determined to be 0.25 nm^2 , which is almost equal to the area of IBVE unit evaluated from the space filling molecular model. This means that at low pressures, the IBVE segments lie essentially flat on the water surface, which is consistent with the n_T dependence of the layer thickness at low pressures (see below).

The surface monolayers were successfully transferred onto a substrate by the vertical dipping method to form a Y-type multilayer film, the thickness of which was determined by surface plasmon resonance²⁾ and transmission electron microscopy³⁾. Both below and above the plateau region, proportionality of the total film thickness to the deposit number as well as transfer ratios close to unity were observed, confirming a good transferability of the monolayer. Figure 2 shows the layer thickness d plotted against n_T . The layer thickness d is apparently constant at 20 mN/m, while it increases linearly with increasing n_T at 35 mN/m.

The above arguments on the n_T dependence of A and d suggest the fine structure of the surface monolayers illustrated in Figure 3; the IBVE segments, which lie essentially flat on the water surface at low pressures, aggregate at higher pressures, forming a

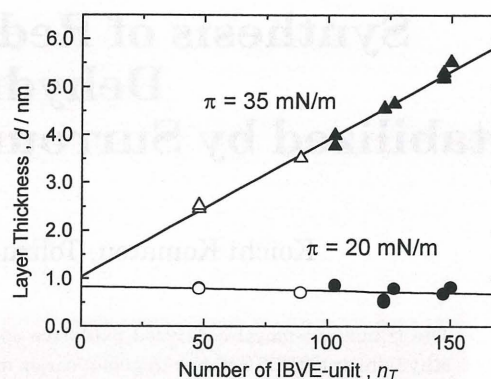


Figure 2. Plots of d vs. n_T for LB films of the block copolymers (open symbols) and the blends (closed symbols) deposited at 20 and 35 mN/m

thicker layer with hydrophobic and hydrophilic segments microphase-separated at the air-water interface. This is consistent with the fact that the surface pressure of the plateau is almost the same as the collapse pressure (22 mN/m) for the PIBVE homopolymer. According to this model, the layer thickness extrapolated to $n_T = 0$ (about 1.0 nm; Figure 2) should correspond to that of the glucose residue-carrying hydrophilic segments: it is thus indicated that the LB film deposited at a high pressure consists of the hydrophilic layer with a thickness of 1.0 nm and the hydrophobic layer with a thickness proportional to n_T .

These results suggest a useful method to control the supramolecular structure of an ultrathin block copolymer film by blending it with a homopolymer; at lower pressures, it is possible to decrease the surface density of the hydrophilic segments in the water, and at higher pressures, where a microphase-separated structure is formed on the water surface (Figure 3b), it is possible to adjust the hydrophobic layer thickness by blending the homopolymer.

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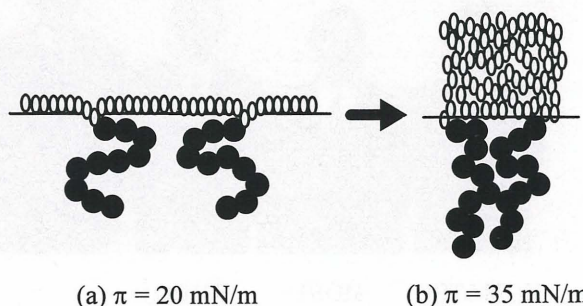


Figure 3. Schematic illustration of monolayers at the air-water interface.